

UDC 666.1.037.97:666.11.01.001.2

USE OF STRUCTURAL CRITERIA FOR CALCULATING OXIDE GLASS COMPOSITIONS FOR HYDROGEN MICROCONTAINERS (A REVIEW)

E. F. Medvedev¹Translated from *Steklo i Keramika*, No. 7, pp. 13–16, July, 2006.

To calculate glass compositions with predictable hydrogen permeability, one should use criteria that determine the structure of material, such as the silica modulus, the cohesion factor, and the structure filling coefficient, as well as the glass comparison coefficient based on the cohesion factor. A graphic method for optimizing numerical values of the specified criteria has been developed. Glass compositions promising for producing hydrogen microcylinders are listed.

Glass has numerous properties, but all of them are just external manifestations of the glass structure. We know from the chemistry of materials that the composition determines the structure and the structure determines the properties. Thus, the structure-forming components SiO_2 , GeO_2 , and B_2O_3 intensify the mechanical properties and chemical resistance of glass, as well as its gas permeability [1–3]. Permeability depends on the packing density of the glass lattice: small ions make it lower, whereas large ions increase it. Permeability in glasses is yet not sufficiently investigated; therefore, an intuitive approach prevails in developing compositions of hydrogen microcylinders (microspheres) for laser thermonuclear synthesis (LTS).

The present study demonstrates the need to use structural criteria in designing microsphere glass compositions in accordance with predicted hydrogen permeability.

Table 1 gives typical glass compositions for microspheres. They are based on SiO_2 , Na_2O , B_2O_3 , and K_2O ; CaO is registered in half of the compositions; other oxides are found occasionally. Based on data analysis, a hypothetical glass composition was composed (mol.%): 67.5 SiO_2 , 12.4 Na_2O , 8.3 CaO , 4.8 B_2O_3 , 4.4 K_2O , 1.0 Al_2O_3 , 0.7 ZnO , 0.5 MgO , 0.3 P_2O_5 , and 0.1 Li_2O . Furthermore, we analyzed the compositions of hollow glass articles that are spontaneously formed in fuel combustion at thermal power plants [8, 9]. Their parameters do not satisfy the LTS standards, but the following composition is promising for chemically resistant microspheres (mol.%): 61.99 SiO_2 , 22.34 Al_2O_3 , 4.06 MnO , 4.86 $(\text{FeO} + \text{Fe}_2\text{O}_3)$, 3.81 K_2O , 1.11 Na_2O , 0.88 TiO_2 , 0.73 CaO , and 0.05 P_2O_5 .

Requirements on geometrical parameters of microspheres for LTS

Diameter D_s , μm	At least 100
Sphericity, % 0.5	
Wall thickness h , μm	At least 0.1
Wall thickness nonuniformity, $\Delta h/h$, %	Not more than 10
Excentricity on the segment $(2-3)h$, %	0.5
Weight nonuniformity, Δm , %	3
Semi-efflux duration of DT gas* $T_{1/2}$, days	At least 30

* DT gas is a mixture of deuterium D and tritium T [10].

There are several known equations for determining the gas flux on glass q and its hydrogen permeability coefficient K_H :

$$q = K_0 A \tau \frac{P_2 - P_1}{h} \quad [11];$$

$$K_H = K_0 \exp\left(-\frac{E}{RT}\right) \quad [5];$$

$$K_H = K_0 T^n \exp\left(-\frac{E}{RT}\right) \quad [12];$$

$$K_H = \frac{rh}{3RT\Delta t} \ln \frac{P_0}{P_0 - P} \quad [13];$$

$$K_H = 0.231 \frac{rh}{T_{1/2} RT} \left(T_{1/2} = 0.693 \frac{\Delta t}{\ln(\Delta N_1 / \Delta N_2)} \right) \quad [13],$$

where K_0 is a constant factor; A is the glass surface area, m^2 ; τ is the gas diffusion duration, sec; P_1 and P_2 is the partial

¹ Russian Federal Nuclear Center (VNIIEF), Sarov, Russia.

TABLE 1

Compo- sition	Molar content, %							Pub- lished source
	SiO ₂	Na ₂ O	B ₂ O ₃	K ₂ O	CaO	Li ₂ O	Al ₂ O ₃	
1	69.68	25.67	—	—	4.65	—	—	[4]
2	76.70	10.60	1.40	—	11.30	—	—	[5]
3	63.60	19.53	16.87	—	—	—	—	[4]
4	78.70	2.70	6.60	12.00	—	—	—	[6]
5	72.40	6.00	4.50	6.00	11.10	—	—	[6]
6	72.70	10.20	7.20	9.90	—	—	—	[6]
7	72.70	21.80	1.80	3.50	—	0.20	—	[5]
8	78.79	18.11	1.49	1.51	—	0.10	—	[5]
9	72.50	14.69	—	0.31	8.24	—	2.04	[4]
10*	79.24	6.82	2.01	0.10	10.03	—	0.20	[7]

* Composition 10 also contained 0.3% P₂O₅, 0.5% MgO, and 0.8% ZnO.

gas pressure on two sides of the glass, Pa; h is the glass thickness, m; E is the gas diffusion activation energy; R is the gas constant; T is the temperature, K; n is a constant (0.5 or 1.0); r is the radius of the microsphere inner cavity, m; Δt is the time of filling it with DT gas, sec; P_0 and P are the internal and external pressure under filling, Pa; $T_{1/2}$ is the duration of the gas pressure decreasing to $0.5P_0$, sec; ΔN_1 and ΔN_2 is the interference band shift when pressure is determined by the optical method.

It is paradoxical that none of the above equations reflect the dependence of the property (permeability) of a material on its fundamental characteristics, i.e., its composition and structure, which are essentially responsible for all properties. Only one paper [7] partly eliminates the said deficiency: the coefficient K_H (mole · m/(m² · sec · Pa)) is expressed as a function of the chemical composition of the glass:

$$K_H = 8.1 \times 10^{-14} \exp \left[-\frac{1}{T} (17,330 - 127.8C) \right], \quad (1)$$

where C is the sum of the molar content of SiO₂, B₂O₃, and P₂O₅, %.

There are as yet no analogues of Eq. (1). However, the authors did not take into account the possibility of introducing other typical glass-forming components, such as BeO and GeO₂, intermediate oxides, and modifiers (their content can be expressed as $100 - C_{\text{SiO}_2 + \text{B}_2\text{O}_3 + \text{P}_2\text{O}_5}$, but then the first three oxides “disappear”). The structural parameters are absent as well. Therefore, Eq. (1) cannot be regarded as sufficiently correct. Let us give an example from [1] of the effect of the composition on the glass structure: Na₂O and B₂O₃ consolidate the structure, whereas SiO₂ loosens it; in sodium-borosilicate glasses these two effects have opposite impacts; with B₂O₃ content around 18 wt.% there is an optimal glass density at which boron changes its coordination number in the presence of Na₂O. The comments on Eq. (1) are given in [14].

Useful information can be extracted from analysis of the dimensionality of the coefficient K_H [7]: $\frac{\text{mole} \cdot \text{m}}{\text{m}^2 \cdot \text{sec} \cdot \text{Pa}}$. Appa-

rently, Pa · sec is nothing else but the measurement unit of dynamic viscosity η : $\text{Pa} \cdot \text{sec} = \frac{\text{N}}{\text{m}^2} \text{sec} = \frac{\text{kg} \cdot \text{m} \text{sec}}{\text{sec}^2 \text{m}^2} = \frac{\text{kg}}{\text{m} \cdot \text{sec}}$. After the measurement unit substitution the coefficient K_H takes the following form: $\frac{\text{mole} \cdot \text{m}}{\text{m}^2 \cdot \text{sec} \cdot \text{Pa}} =$

$$\frac{\text{mole} \cdot \text{m} \cdot \text{m} \cdot \text{sec}}{\text{m}^2 \text{kg}} = \frac{\text{mole} \text{ sec}}{\text{kg}} \frac{\text{m}^2}{\text{m}^2}.$$

If kg/mole, m²/sec, and m² are the measurement units of the molar mass M of the gas diffusing via the glass, the gas diffusion coefficient D , and the spherical surface area S , respectively, then

$$K_H = \frac{S}{MD}.$$

The molar mass of hydrogen is 2015.8 kg/mole; therefore,

$$K_H = 0.0005 \frac{S}{D}. \quad (2)$$

Let us assume that microspheres are made from quartz glass (100% SiO₂) and silicate glass (below 100% SiO₂). The parameters D and S in both cases can be equal, since expression (2) does not contain a correlation between K_H and the molar content of oxides, but in that case the permeability coefficients of quartz and silicate glass have to be equal as well. However, this contradicts the actual fact: quartz glass is the most gas-permeable among oxide glasses [1, 3].

Let us consider glasses with different silica modulus taking quartz glass as the extreme case: Na₂O · SiO₂, Na₂O · 2SiO₂, Na₂O · 3SiO₂, ..., SiO₂. The structure of glass in the presence of the modifier Na₂O gradually changes from a one-dimensional pattern with two-dimensional fragments to a two-dimensional pattern with 3D fragments and then to a 3D structure in the extreme case with 100% content of SiO₂. It is obvious that as the composition and the structure of glass change, its property (gas permeability) changes as well; consequently to avoid the “anonymity” of glasses we need a criterion of their qualitative differences in composition and structure. For this purpose we can use the structure cohesion factor proposed by N. N. Ermolenko [15]:

$$Y = \frac{\sum_j x_j C_j z - \sum_k x_k C_k}{\sum_j x_j C_j}, \quad (3)$$

where $x_{k(j)}$ is the number of atoms in an oxide molecule; j are atoms with the number of bonds larger than unity; k are

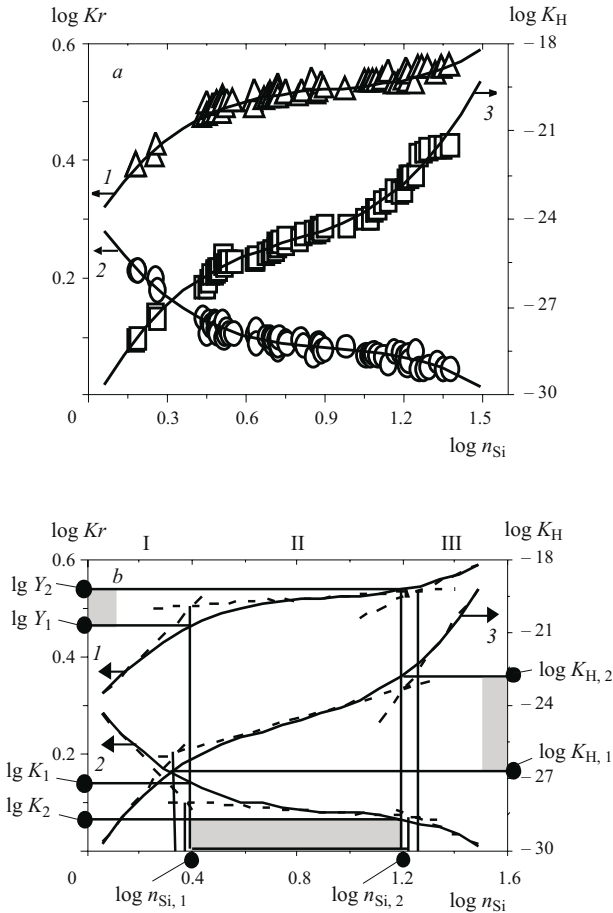


Fig. 1. Variations of structural criteria $\log Kr$ of glasses depending on silica modulus n_{Si} : *a*) $\log Y$, $\log K_H$, $\log K$; *b*) geometrical constructions; 1) $\log Y = f(\log n_{Si})$; 2) $\log K = f(\log n_{Si})$; 3) $\log K_H = f(\log n_{Si})$; bold-type dots indicate $\log n_{Si}$, $\log Y$, $\log K_H$, and $\log K$ found by geometrical constructions; I – III) criteria variation areas found by the tangent method.

atoms with the number of bonds equal to unity; z is the valence of atoms comprising the oxides.

Equation (3) takes into account both the structure and the composition of glass; Y determines the average number of bridge oxygen atoms in structural polyhedrons; a three-dimensional lattice is formed with $Y = 4$, two-dimensional layers — with $Y = 2$, and a one-dimensional chain — with $Y = 2$. With $Y < 2$, a continuous skeleton is not formed and the formation of glass is impossible; hence we obtain the glass formation condition based on the data from [1, 3]:

$$2 < Y < 4. \quad (4)$$

The corresponding structural fragments are described in [15]. If we add the factor Y to Eq. (2)

$$K_H = 0.0005 \frac{S}{D} Y,$$

it is easy to see that the permeability of quartz glass ($Y = 4$) is indeed higher than of silicate ($Y < 4$) glass; accordingly,

microspheres should not be made of quartz. In fact

$$K_{H, SiO_2} = 0.0005 \times 4 \frac{S}{D} = 0.002 \frac{S}{D},$$

$$2 \leq Y < 4 \rightarrow Y \neq 0;$$

then

$$K = \frac{K_{H, SiO_2}}{K_{H, g}} = 4Y^{-1} > 1 \text{ always}, \quad (5)$$

where K is the glass comparison coefficient; K_{H, SiO_2} and $K_{H, g}$ are the coefficients of hydrogen permeability of quartz glass and any other glass, respectively.

Thus, we have identified the “anonymity” of various types of glasses concealed in Eq. (1) and have proposed a criterion to eliminate it, namely, the glass comparison coefficient K .

When designing glass compositions, their glass permeability can be controlled by varying the molar volumes of the oxides in their structure [14]. The sum of the molar volume of the modifiers and intermediate oxides ΣV_i should not exceed the total molar volume of the glass forming agents ΣV_{GF} . On defining the ratio $\Sigma V_i : \Sigma V_{GF}$ as the structure filling coefficient, the glass forming condition for the production of glass microcontainers is as follows:

$$0 \leq 1 - \Sigma V_i / \Sigma V_{GF} < 1 \text{ for } 0 < \Sigma V_i \leq \Sigma V_{GF}. \quad (6)$$

Let us consider an example of development and optimization of glass compositions using structural criteria, such as the silica modulus, the molar volumes of the oxides, and the structure cohesion factor. The data from Table 1 were not sufficient; therefore, we selected 79 glasses from a reference book [5], whose qualitative composition, the content of the main components, and some other parameters are close to the desired composition.

The silica modulus n_{Si} was calculated based on the known formula [16] (the modulus notation has been changed to avoid confusion with the notation of molar mass M):

$$n_{Si} = \frac{C_{SiO_2}}{C_{Na_2O}}.$$

This modulus defines the ratio of the main components of silicate glasses (SiO_2 and Na_2O) that form a structural lattice; therefore, it is a structure-determining criterion.

Using Eqs. (1), (3), and (5) we calculated the hydrogen permeability coefficient, the structure cohesion factor, and the coefficient for comparing the permeability of quartz glass and an arbitrary glass; the method in [17] was used to calculate the molar volumes of the components. The consistent variation of the curves (Fig. 1a) is explained by the fact that the criteria K_H , Y , and K depend on a common fundamental

parameter, i.e., the chemical composition:
 $K_H = f(C)$, $Y = f(C)$, $K = f(Y) = f(C)$.

Using the tangent method (or the analytical geometry method), we split each curve into three segments (I, II, and III, Fig. 1b). By plotting perpendiculars to the abscissa axes we determined the coordinates of the tangent intersection points. Range III contains compositions with a high content of glass-forming agents and corresponds to higher silica modulus and the maximum permeability; therefore, it is unsuitable for glass microsphere compositions. Range I correlates with a low structural cohesion factor ($Y \leq 2$), accordingly, there is high probability of obtaining ceramics rather than glass. Range II of the variation of n_{Si} and K_H with $2 \leq Y < 4$ is the most suitable for developing glasses.

The gray shading on the abscissa axis indicates the domain that is common for all curves. Perpendiculars were plotted from the extreme points (the limiting values of silica modulus variation) until the intersection with the curves $\log Y = f(\log n_{Si})$ and $\log K_H = f(\log n_{Si})$; then perpendiculars were constructed from the intersection points to the left and right ordinate axes, thus defining the areas of variation of the criteria Y and K_H for the glasses that are being designed. Note that, depending on the silica modulus, oxides may have an ambiguous effect on glass permeability (which is discussed in detail in [18]), i.e., in the case of a different silica modulus the same quantity of an oxide in glass may either strengthen or weaken the glass structure; accordingly, the permeability either grows or decreases.

After that we selected the most suitable values from each pair of V_i values and calculated the mass content of the oxides [18] by multiplying the molar volumes of V_i by their densities ρ_i (obtained from the reference literature). Then the composition was verified for satisfying boundary conditions (4) and (6) and the admissible silica modulus variation; the latter is determined depending on the glass synthesis technology (the classical or the sol-gel method). This procedure was used to develop and optimize glass compositions for producing microspheres. The developed glass compositions are given in Table 2. The batches were synthesized in an aqueous medium; therefore, the optimum value for the selected technology is $1.0 \leq n_{Si} < 3.5$; the bottom limit was determined by analyzing the phase diagram of the $Na_2O - SiO_2$ system, and the upper limit was found empirically.

It should be noted that the properties of a material are not identical to the properties of a product made of this material; they correlate as a function and its limit. The property of a material is a theoretically possible value, whereas the property of a product is a practically attainable parameter. Various mechanical defects, such as surface cracks, prevent reaching an ideal property in the product. Therefore, one should impose high requirements on the composition analysis and accuracy in complying with the technological requirements.

TABLE 2

Component	Weight content, %, * based on patent data			
	[19]	[20]	[21]	[22]
H ₃ BO ₃	8.21 – 8.31	7.64 – 7.82	7.46 – 7.82	5.56 – 7.44
NaOH	27.60 – 27.72	26.46 – 26.72	25.43 – 26.59	13.60 – 15.52
KOH	11.01 – 11.14	10.25 – 10.48	10.01 – 10.36	0.06 – 0.15
Li ₂ SO ₄	0.07 – 0.70	–	–	–
Li ₂ CO ₃	–	0.22 – 0.74	0.25 – 0.74	–
Eu ₂ O ₃	–	0.70 – 4.00	0.70 – 4.00	–
PbO	–	–	–	6.65 – 6.82
C ₆ H ₈ O ₇	–	3.90 – 22.30	3.90 – 22.30	20.50 – 22.90
C ₂₂ H ₁₁ O ₉ (NH ₄) ₃	–	–	0.60 – 3.50	0.10 – 0.24
(NH ₂) ₂ CO	–	1.00 – 3.00	1.00 – 2.90	–
CaCO ₃	–	–	–	5.94 – 6.06
Mg(OH) ₂	–	–	–	1.17 – 1.45
Al(OH) ₃	–	–	–	0.02 – 0.05

* Remainder H₂SiO₃.

Thus, structure-determining criteria should include the silica modulus, the cohesion factor, and the structure filling coefficient. A new criterion has been introduced, namely, the glass comparison factor taking into account the structure cohesion factor. A graphic method has been developed for optimizing the structural criteria for subsequent development of glass compositions for hydrogen microspheres.

REFERENCES

1. V. Eitel, *Physical Chemistry of Silicates* [Russian translation], IL, Moscow (1962).
2. M. M. Shul'tz and O. V. Mazurin, *Contemporary Concept of Glass Structure and Properties* [in Russian], Nauka, Leningrad (1988).
3. V. A. Sharagov, *Chemical Reaction of Glass Surface with Gases* [in Russian], Shtiinza, Kishinev (1988).
4. V. V. Budov, "Hollow glass microspheres. Application, properties, technology," *Steklo Keram.*, No. 7 – 8, 7 – 11 (1994).
5. A. A. Appen, M. S. Aslanova, N. P. Amosov, et al., *Glass: a Reference Book* [in Russian], Stroiizdat, Moscow (1963).
6. V. V. Budov and L. S. Egorova, "Glass microballs. Application, properties, technologies," *Steklo Keram.*, No. 7, 2 – 7 (1993).
7. P. T. Tsugawa, J. Moem, P. E. Roberts, and P. G. Souers, "Permeation of helium and hydrogen from glass microsphere laser targets," *J. Appl. Phys.*, **47**(5), 1987 – 1993 (1976).
8. L. Ya. Kizel'shtein, I. V. Dubov, A. A. Shpitsgluz, and S. G. Parada, *Components of Ash and Slag from Thermal Power Plants* [in Russian], Energoatomizdat (1995).
9. E. F. Medvedev, "Hydrogen permeability of microspheres produced from ash and slag," *Steklo Keram.*, No. 11, 12 – 15 (2002).
10. Yu. A. Merkul'ev, *Laser Thermonuclear Targets. Development of Physical Principles for Production Technology and Instruments For Their Production. Author's Abstract of Candidate's Thesis* [in Russian], Moscow (1996).
11. V. K. Leko and O. V. Mazurin, *Properties of Quartz Glass* [in Russian], Nauka, Leningrad (1985).
12. J. E. Shelby, *Introduction to Glass Science and Technology*, Cambridge (1997).

13. A. V. Veselov, A. V. Dudin, G. V. Komleva, and Yu. D. Pukhov, "The interference method for gas control in LTS targets," *Kvant. Elektron.*, **8**(5), 1111 – 1114 (1981).
14. E. F. Medvedev, "The choice of structural parameters in designing chemical compositions of glass microspheres," *Steklo Keram.*, No. 7, 8 – 11 (2001).
15. N. N. Ermolenko, "Chemical structure and some properties of oxide glasses," in: *Vitreous state. Proc. of VIII All-Union Conf. on Vitreous State* [in Russian], Nauka, Leningrad (1988), pp. 132 – 139.
16. R. Iler, *Chemistry of Silica*, Wiley, New York (1979).
17. M. A. Matveev, G. M. Matveev, and B. N. Frenkel', *Calculations in Chemistry and Technology of Glass. Reference Book* [in Russian], Stroiizdat, Moscow (1972).
18. E. F. Medvedev, "Calculation of glass microsphere compositions," *Steklo Keram.*, No. 8, 3 – 6 (2002).
19. E. F. Medvedev and B. N. Ilyushechkin, *A Solution for Producing Hollow Glass Microspheres. RF patent No. 2036171* [in Russian].
20. E. F. Medvedev and B. N. Ilyushechkin, *A Solution for Producing Hollow Glass Microspheres. RF patent No. 2036856* [in Russian].
21. E. F. Medvedev and B. N. Ilyushechkin, *A Solution for Producing Hollow Glass Microspheres. RF patent No. 2033978* [in Russian].
22. E. F. Medvedev, *A Solution for Producing Glass Microspheres. RF patent No. 2205802* [in Russian].